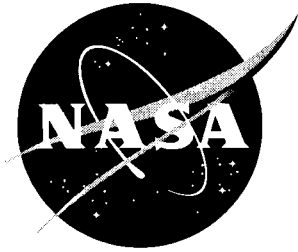


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Tensile Properties of a Cellulose Ether Hydrogel

Jeffrey A. Hinkley
Langley Research Center, Hampton, Virginia

Stevin H. Gehrke
Kansas State University, Manhattan, Kansas

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23681-2199

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Jeffrey A. Hinkley
Advanced Materials and Processing Branch
NASA Langley Research Center
and
Stevin H. Gehrke
Department of Chemical Engineering
Kansas State University

Abstract

Poly(hydroxycellulose) solutions were molded into dumbbell-shaped specimens crosslinked with divinyl sulfone. The resulting hydrogels were tested in tension at room temperature and also at a temperature above the 40°C shrinkage transition. In contrast to behavior seen in some other responsive gels, apparent initial tangent moduli were lower in the shrunken state; breaking elongations were significantly higher. Possible molecular mechanisms are suggested, and implications for the design of temperature-responsive actuators ("artificial muscles") from this material are discussed.

Introduction

The ability of certain solvent-swollen, crosslinked polymers to respond to changes in temperature, pH, illumination, and other physical and chemical stimuli [1] has earned these gels consideration as "artificial muscles" [2,3]. To be useful in this application, the materials will have to undergo relatively large changes in dimensions and they will have to support load. This Memorandum is a report on initial experience with large-strain tensile characterization of a relatively fragile water-swollen (hydrogel) material. The eventual goal is to understand how mechanical strength and toughness can be built into a gel without sacrificing other desired properties.

The variables available to the synthetic chemist are the polymer concentration, the degree of crosslinking, and the nature of the polymer backbone (e.g. its chain flexibility or solubility). Very little guidance is available on how to use these to create a tough, strong material, since large-strain behavior of gels is rarely even reported [4]. Some exceptions include work on gelatin [5] and other food gels [6], some characterization of soft gels applicable for in-vitro cell growth studies [7], and toughness determinations on commercial contact lens materials [8].

A few papers on the tensile properties of responsive gels have begun to appear [9,10]. Among gels that can respond to their environment, protein gels [11] are of particular interest because the response has been regarded as a model for a wide variety of biological energy transduction processes [12], and even as the origin of motility and of action potentials in living cells [13]. Also of interest is the role of protein secondary structure (chain conformation) in controlling gel properties [14].

For the present study, a semisynthetic polysaccharide backbone was chosen because it is relatively inexpensive and several molecular weight grades are readily available in

good purity. Dilute aqueous solutions of this polymer, hydroxypropylcellulose, phase separate above 40°C [15]; when crosslinked, it forms a temperature-responsive hydrogel that shrinks over a rather narrow temperature range [16].

Experimental

Hydroxypropylcellulose, HPC, (Aldrich, mol wt= 10^5) was dissolved at 10% or 20% by weight in deionized water by gentle overnight stirring. Gels will be identified by the concentration of this solution. Divinyl sulfone (97%, Aldrich) crosslinker was added (0.18 g/g polymer) and the solution was thoroughly stirred by hand. NaOH (1M) was then added to bring the solution to ca. pH 12. The solution was centrifuged to remove air bubbles that had been introduced by the stirring, then poured into silicone molds capped with glass plates (Figure 1). Gelation occurred in a matter of minutes. The reaction was allowed to proceed at room temperature for 18-24 hours. After that, the specimens were immersed in dilute HCl and then stored in deionized water. Degree of swelling was determined by blotting and weighing samples equilibrated at the test temperatures and drying them to constant weight.

Tensile specimens were molded as scaled-down versions of a tapered geometry routinely used for rubber testing (ASTM D638, type V); gage sections were 0.8 x 1.5 x 18mm. For testing, each specimen was glued to a polyester film frame using cyanoacrylate adhesive. The frame supported the gel during mounting in the test stand and could be gripped easily; the sides of the frame were cut just before testing (Figure 2). Testing was conducted at 1.3 cm/min crosshead speed in a misting chamber designed to expose the specimen to a continuous spray of deionized water; a thermistor probe verified the temperature of the spray. Strain was not measured directly, so approximate stretch ratios were calculated from the crosshead displacement and the length of the straight section of the specimen.

Results and discussion

Preliminary experiments with small pieces of HPC gels prepared in this manner showed that when heated, the samples turned from clear to opaque white and expelled water. Shrinkage occurred between 25 and 50°C (Figure 3), so temperatures of 22 and 55°C were chosen for tensile testing below and above the transition. Table 1 summarizes gel concentrations determined on actual specimens after testing.

**Table 1. Equilibrium swelling:
Polymer content of gels at test temperatures.**

Nominal (synthesis) concentration	Concentration at 22°C	Concentration at 55°C
10%	9.9%	56.8%
20%	20.8%	51.4%

According to classical Flory-Rehner theory [17], the equilibrium degree of swelling of a rubber network is related to the average molecular weight of the network chains, M_c . Using room temperature polymer-solvent interaction parameters, χ , quoted in reference [18], one calculates $M_c=51$ kg/mol and 11 kg/mol, for the 10% and 20% gels, respectively. These values should not be taken too literally for two reasons. Firstly, they are very sensitive to the assumed value of χ , which depends on concentration, temperature, and chemical structure. Most commercial HPC has a stated “molar substitution” of about four hydroxypropyl residues per anhydroglucose unit, but the exact substitution of our samples is not known. Secondly, the chains of cellulose and its derivatives are known to be quite rigid [19]; a network chain of the size calculated would contain at most a few Kuhn statistical segments, so the theory for random coils probably does not apply. The calculation does serve to show that the crosslinking reaction was more efficient at the higher synthesis concentration, leading to a more tightly crosslinked gel network.

Figures 4 and 5 show force-elongation curves in tension for the 10% gel. Data for a number of specimens are superimposed to give an idea of the degree of variability. Despite the scatter, a clear qualitative difference in the shapes of the curves emerges between 22° and 55°C. At the higher temperature, the initial slope is smaller, there is an extended plateau in the load, and the elongation at break is much higher. Representative curves are replotted in Figure 6 to show the difference more clearly. Figure 7 is the corresponding plot for the 20% gel. For this material, a well-defined plateau is absent at 55°C, but an inflection is apparent. The curves themselves were found to be more consistent at this higher concentration.

The intriguing plateau in the stress-strain behavior is very much like that seen previously for HPC gels in an organic solvent [20], and attributed by those authors to a strain-induced isotropic-to-nematic phase transformation. This would be akin to, but not as distinct as, that predicted for unswollen nematic liquid crystal elastomers [21]. At 55°C, our gels have expelled enough water to be above the (room-temperature) critical concentration for formation of a cholesteric mesophase [22]. This might explain the unusual load-elongation curve. In reference 20, the concentration of polymer in the gel was varied, and the plateau was only seen over a certain range of concentrations. A *temperature-induced qualitative change* in stress-strain behavior does not seem to have been reported before, and would certainly need to be characterized in an actuator (artificial muscle) application.

Even if the high-temperature phase is not liquid-crystalline, a collapsed polymer chain in a poor solvent may exhibit a coil-globule transition [23, 24]. It has been proposed that stretching of such a chain could occur not by uniform elongation, but by chain segments “reeling out” [25] from the globule. Studies on other gels would be helpful in clarifying the origin of the change in mechanical behavior.

Regardless of the mechanism, the response of HPC gels leads to interesting implications for the design of devices that might use the shrinkage transition. In Figure 8, the load-elongation curve of the swollen gel is shifted so that the loads are shown relative to the unstretched length of the *shrunk* gel. Using this plot, we can predict how a gel specimen would behave under a fixed load. At very low loads, below the load where the two curves cross, the shrinkage transition would cause the sample’s length to

decrease (moving to the left horizontally from the 22° curve to the 55° curve). At higher loads, on the other hand, (above ~2.4 g), a sample initially at 22° will *lengthen* if it is heated to 55°. The latter behavior was in fact observed upon heating specimens in water under dead-weight loads. The length change was reversible within a few percent; i.e., any effect of creep (over the period of several hours that the sample was under load) was minor compared to the overall response.

For completeness, mean tensile properties (Table 2) were calculated from the force-displacement curves. To do this, the data were normalized for the specimen cross-sectional area and gauge length, assuming additivity of volumes and isotropic swelling. Uncertainties given in the table are due to experimental scatter among five replicates.

Table 2. Engineering tensile properties (average and standard deviation)

Test temperature, °C	Nominal (synthesis) concentration	Initial (tangent) modulus, kPa	Elongation at break, percent	Tensile strength, kPa
22	10%	67±6	51±17	58±33
55	10%	56±15	288±40	228±105
22	20%	765±50	15±1	130±15
55	20%	66±42	78±13	87±17

Looking first at the room temperature data, we see that the sample with the higher polymer content has a higher modulus than the more dilute network. The primary effect is not one of dilution, however, but of crosslink density, as was already mentioned. The tensile strength is also higher for the 20% network. This could not have been predicted *a priori*, however, given that strength as a function of crosslink density probably goes through a maximum [26]. It should probably be emphasized that as a practical matter, the 20% gel broke more easily during room-temperature handling than did the 10% gel, despite the former's greater strength. Presumably this reflects its lower elongation at break. The importance of failure strain in the ability to manipulate gels does not seem to have been sufficiently recognized [4].

The increased elongation at break in both compositions at 55° is characteristic [27] of what are called "supercoiled" networks (e.g. those produced by drying polymer networks that were crosslinked in the swollen state). Supercoiling would also result if solvent (in this case water) was expelled due to a decrease in solubility of the polymer. The 10% gel was not only more ductile at the higher temperature but also, as it turns out, substantially stronger. We note that one of the polypeptide gels in reference 6 was above a shrinkage transition (attributed in that case to "hydrophobic folding") and possessed noticeably better strength, toughness, and handling qualities at room temperature.

Finally, note that between room temperature and 55°C, the modulus decreased for both compositions. This was somewhat unexpected: reference 6 showed a gradual modulus

increase with temperature for elastin-like gels and reference 28 describes an 18-fold modulus increase on transitioning to the high-temperature, shrunken state of poly(N-isopropyl acrylamide) hydrogel. Takigawa *et al.* [28] attributed the latter change to the formation of physical crosslinks (in addition to the chemical crosslinks introduced during the synthesis). What seems clear from comparing these three polymers is that superficially-similar phase changes can lead to rather different mechanical properties trends in gels.

Conclusions

Procedures have been developed to test small samples of temperature-responsive hydrogels. In HPC gels, the temperature-induced phase change produced a qualitative change in the stress-strain behavior that would affect their use as an "artificial muscle" or in other load-bearing applications.

Stiffnesses, strengths, and failure strains in shrunken HPC gels cannot be predicted from data on the swollen state. A change in the molecular deformation mechanism is thought to accompany the phase change.

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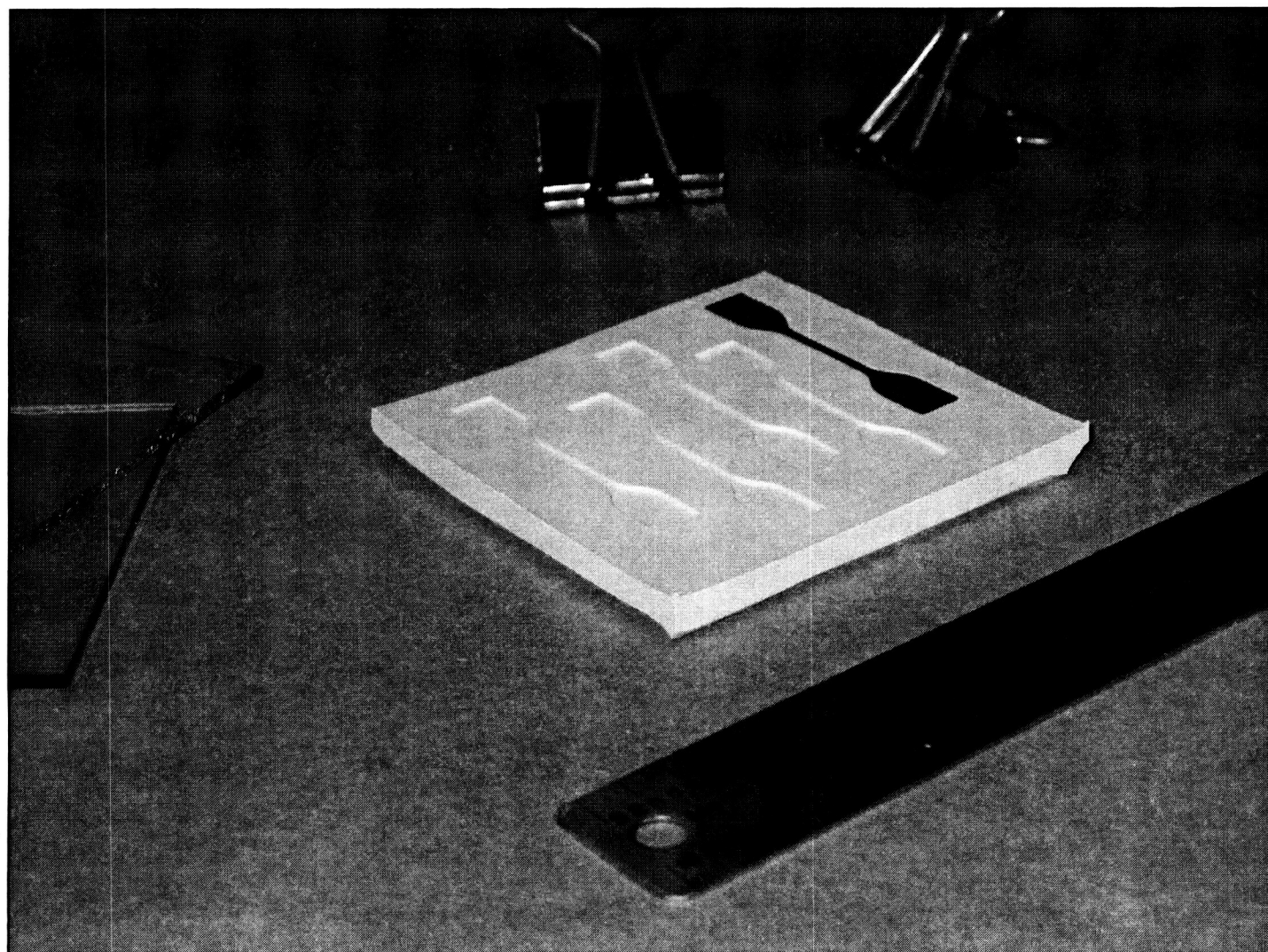


Figure 1. Silicone rubber mold used to fabricate tensile specimens

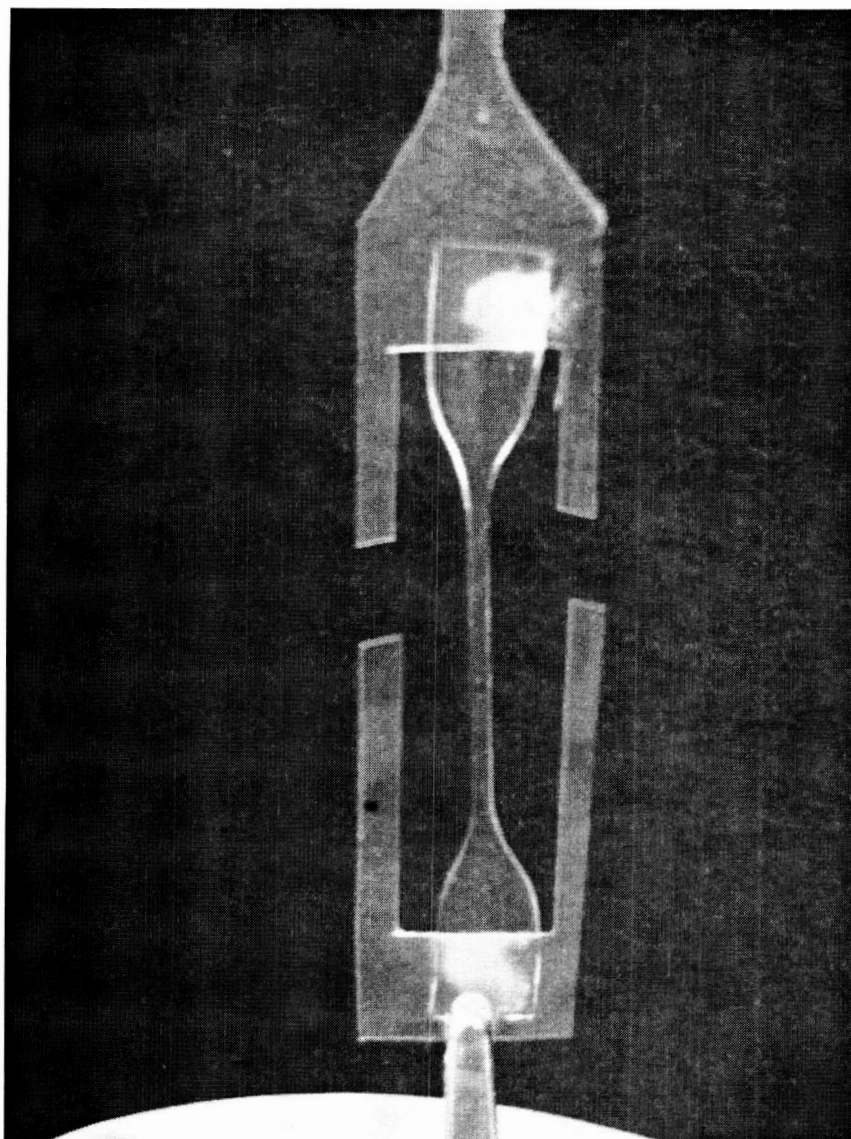


Figure 2. Gel specimen under test at 22 C.

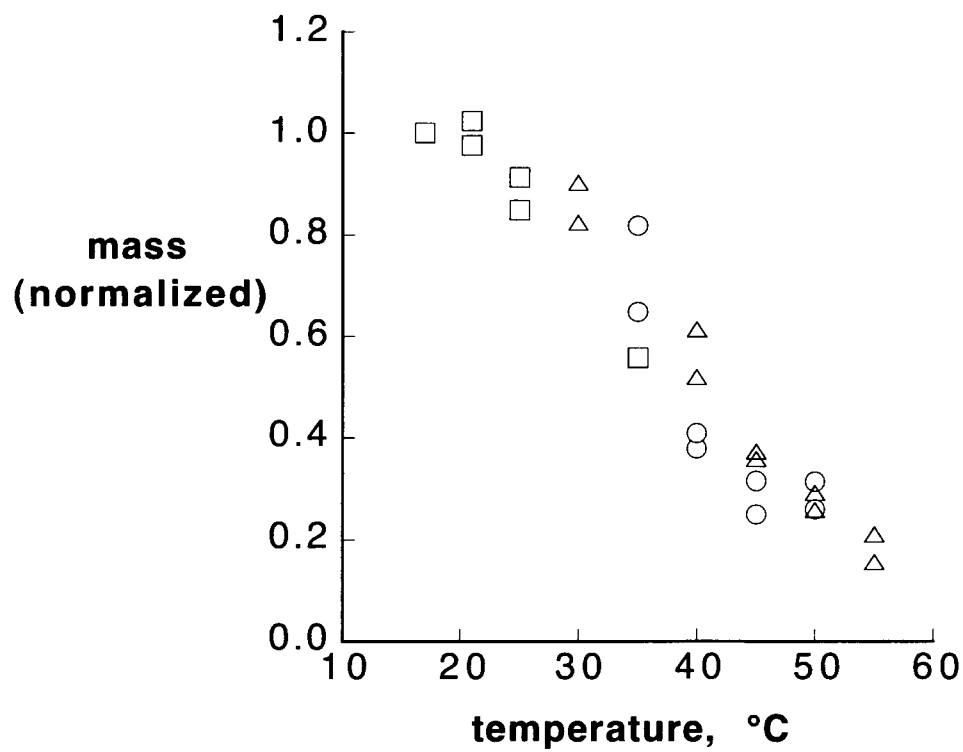


Figure 3. Equilibrium swelling: mass of HPC gel samples (normalized to value at 17°C).

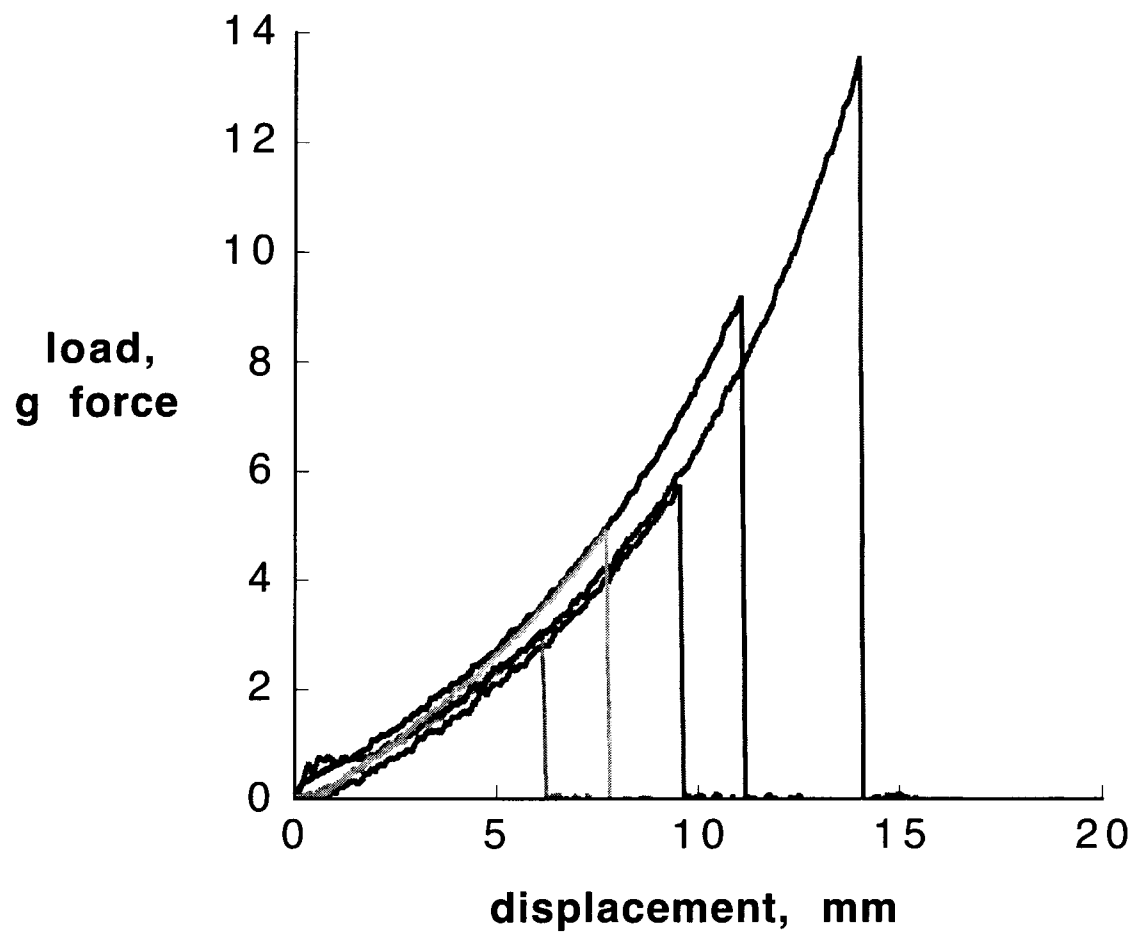


Figure 4. Load-displacement curves for 10% gel at 22°C.

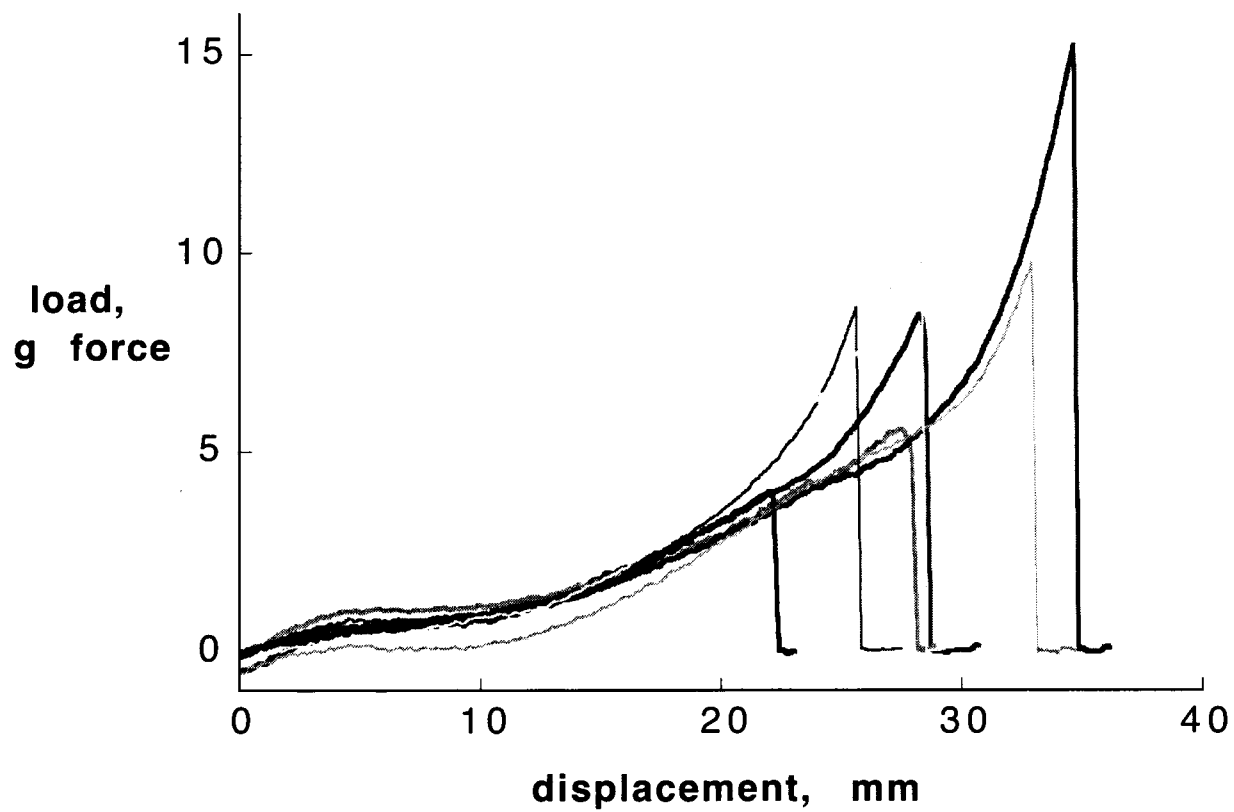


Figure 5. Load-displacement curves for 10% gel at 55°C.

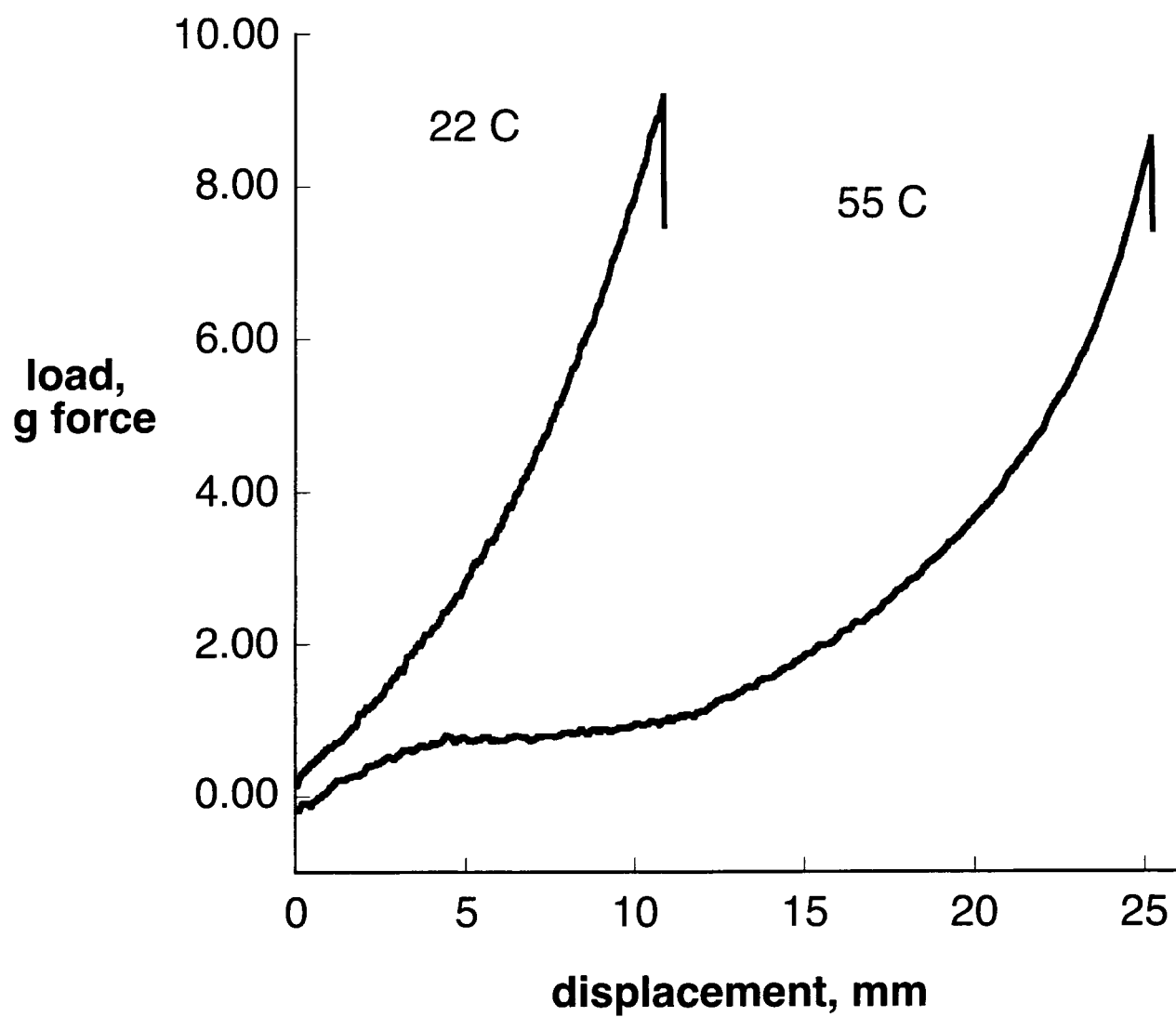


Figure 6. Comparison of tensile behaviors of 10% gel at two test temperatures.

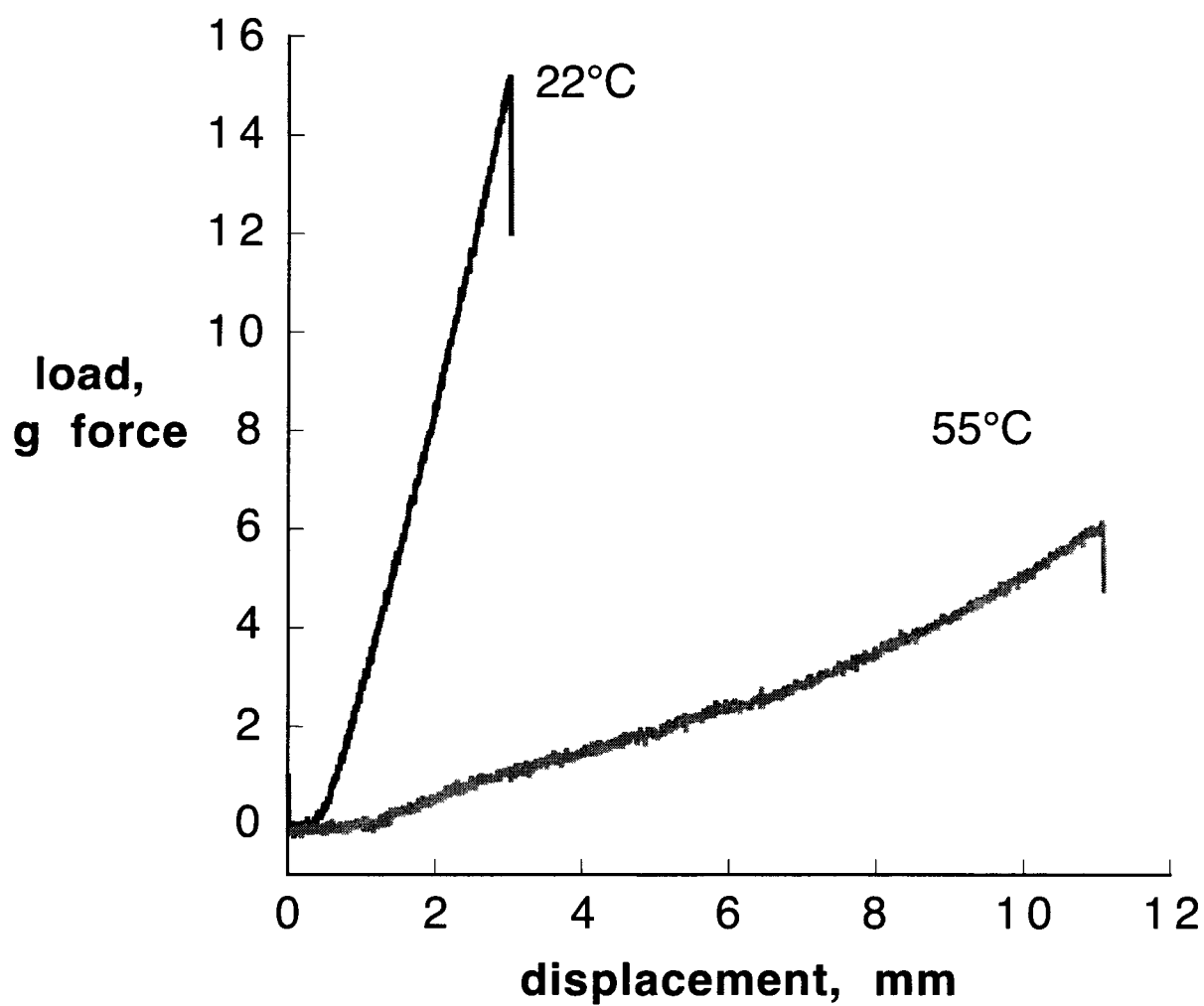


Figure 7. Comparison of tensile behaviors of 20% gel at two test temperatures.

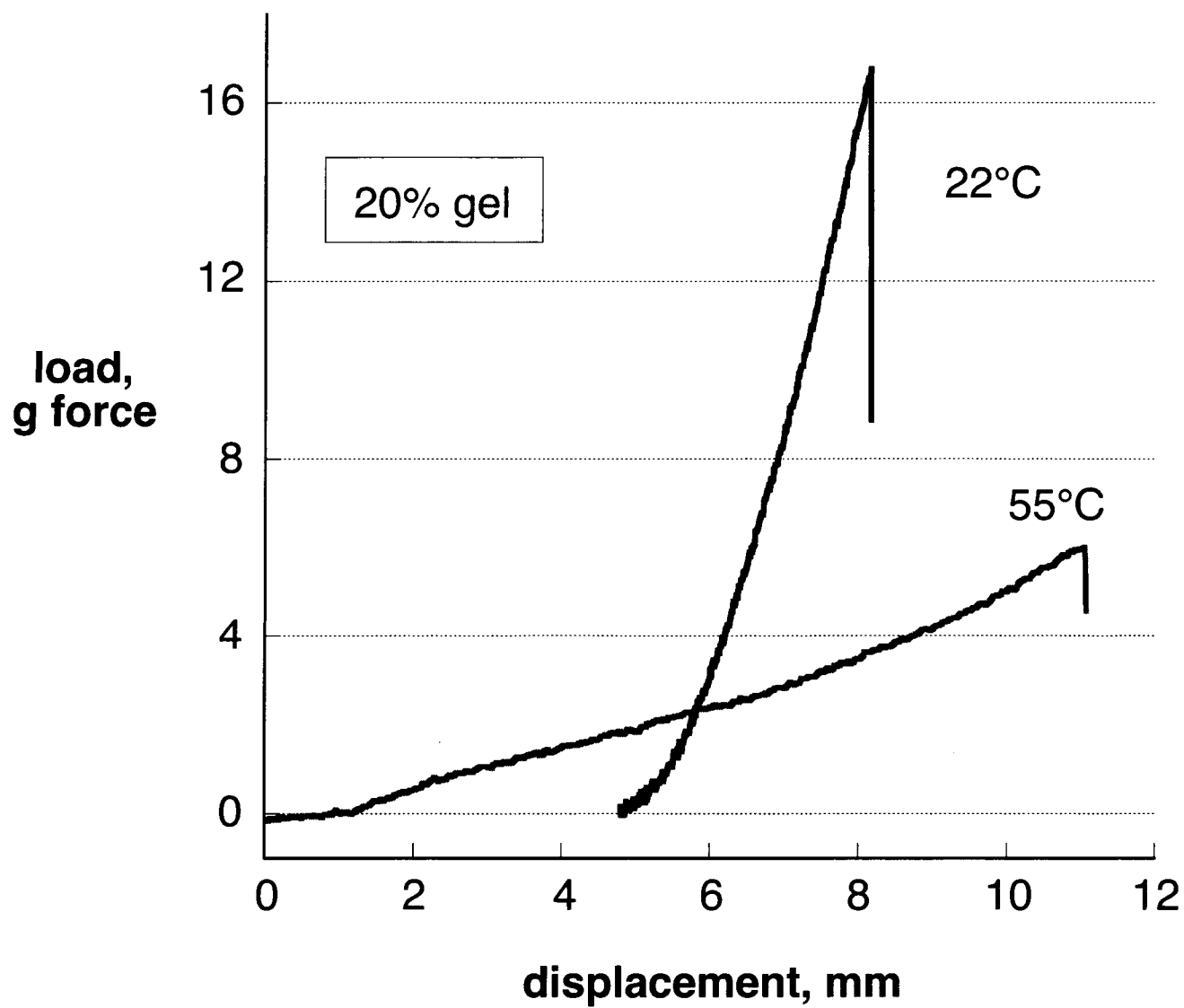


Figure 8. Tensile curves for 20% gel offset to show length at two temperatures.

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